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LAYER STRUCTURES

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# COMPARISON OF EPITAXIAL GROWTH TECHNIQUES
# FOR III-V LAYER STRUCTURES

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## ABSTRACT

Epitaxial processes are essential for the growth of III/V alloy semiconductors for electronic and photonic devices. For the growth of elaborately structured materials such as heterojunctions, quantum wells, and superlattices for the fabrication of the most advanced electronic and photonic devices, in particular, vapor phase growth processes have become standard. This paper will deal specifically with the epitaxial (mainly vapor phase) growth of III/V semiconductor materials. The approach taken here is somewhat non-traditional due to the recent hybridization of both precursor molecules and growth techniques. The distinctions between the various growth techniques are traditionally based on the nature of the precursor molecules. Chloride VPE uses chloride group III and and group V molecules and hydride VPE uses hydride group V precursors, while organometallic vapor phase epitaxy uses organometallic group III precursors and either hydride or organometallic group V precursors. Recently, we have developed group III precursors with *both* organic and Cl radicals on the same molecule. Similarly, group V precursors containing both organic and H radicals have been developed. Thus, it is unclear whether the techniques using such molecules should be called organometallic, chloride, or hydride VPE. The emphasis of this paper will be on more fundamental distinctions between the various techniques, with particular attention to the characteristics of the precursor molecules, themselves. An attempt is made to retain the traditional names, as far as possible, although recently-developed hybrid techniques such as metalorganic molecular beam epitaxy, gas source molecular beam epitaxy, and chemical beam epitaxy will also be described. This paper will present a review of our current understanding of the fundamental strengths and weaknesses of the various growth techniques as well as a comparison of the properties of the highest quality materials and structures produced by each technique.

## I. INTRODUCTION

A virtual revolution in semiconductor device design has been spawned by the invention of heterostructures, quantum wells, superlattices, and similar structures. These advanced structures have led to significant advances in the performance of many devices, including lasers, light emitting diodes, detectors, and both field effect and bipolar transistors. Such structures can only be produced by epitaxial growth processes. These applications place stringent demands on the growth technique, including: high purity, low defect density, abrupt interfaces for heterostructures and superlattices, controlled doping profiles, economy (large scale with high yield, i.e., high uniformity and

**92-13850**

1

reproducibility), and safe operation. Several epitaxial growth techniques have been used for semiconductors, including liquid phase epitaxy (LPE), chloride vapor phase epitaxy (ClVPE) using chlorides of both the group III and V elements, hydride vapor phase epitaxy (HVPE) using chloride group III elements combined with group V hydrides, organometallic vapor phase epitaxy (OMVPE) using organometallic group III elements combined with either hydride or organometallic group V elements, and molecular beam epitaxy (MBE) using elemental group III and group V sources. The latter two techniques have also been hybridized, resulting in gas source MBE (GSMBE), organometallic MBE (OMMBE or MOMBE), and chemical beam epitaxy (CBE).

## II. LIQUID PHASE EPITAXY

The first technique listed, LPE, was one of the first techniques used for the growth of high purity epitaxial layers of III/V materials. Its early popularity was related to the simplicity of the technique and the high purity levels obtained. This is mainly due to the use of elemental starting materials, which have been available in high purity form for several decades. LPE also has several significant disadvantages, especially for large-scale, high-yield processes. As indicated in Fig. 1, LPE is not capable of the growth of certain alloys, notably those containing Al and In together.[1] There also difficulties with uniformity and surface morphology of layers grown by LPE. Even more deleterious is the inability to produce abrupt interfaces for quantum well and superlattice structures. For these reasons, LPE is normally discounted for the growth of large area layers containing atomically abrupt interfaces. Even though LPE was one of the leading epitaxial growth techniques for III/V semiconductors during the 1970's, research in this area has slowed to a trickle during the last decade. It is still a leader in terms of material purity and the ability to grow thick (>10 μm) epitaxial layers. However, for controlled growth of many materials and the superlattice structures required for today's devices vapor phase processes are normally used. In an effort to compare the various techniques, the electron mobilities for the highest purity GaAs and InP are compared in Fig. 2. This is a popular approach to comparing the capabilities of various epitaxial growth techniques. Recognizing that this sometimes has little to do with the *intrinsic* capabilities of the individual processes, we attempt to make such a comparison in Fig. 2. Many of the results listed are discussed in Reference 2. Only the most recent results are discussed in the appropriate sections of this paper. Both GaAs and InP purities in layers grown by LPE are acceptable, although other techniques have produced higher 77K mobilities for both. Since LPE is not suitable for the production of structures giving high mobility two-dimensional electron gas structures, no entry is made in this column.

## III. PRECURSORS for VAPOR PHASE EPITAXY

The great variety of vapor phase epitaxial processes for the growth of III/V semiconductors is indicated in Fig. 3. The only physical technique, defined as a technique not involving molecular precursors, capable of producing single crystalline materials is MBE. Taking the broad view necessary to encompass the diverse vapor phase growth techniques involving chemical vapor transport

2

| Technique | Strengths | Weaknesses |
|---|---|---|
| LPE | Simple<br>High Purity | Scale-Economics<br>Inflexible<br>Morphology/Uniformity<br>Graded Interfaces<br>Al/In Alloys Difficult |
| ClVPE | Simple<br>High Purity | Al Alloys Impossibe<br>Sb Alloys Difficult<br>$\geq20$Å Interface Widths |
| HVPE | Well-Developed<br>High Purity | Al Alloys Impossibe<br>Sb Alloys Difficult<br>$\geq20$Å Interface Widths |
| MBE | Simple Chemically<br>Uniform<br>Abrupt Interfaces<br>In-Situ Diagnostics | As/P Alloys Difficult<br>"Oval" Defects<br>Expensive (Capital)<br>Low Throughput<br>Poor InP |
| CBE | Versatile<br>Uniform (expected)<br>Abrupt Interfaces<br>In-Situ Diagnostics | Carbon Contamination<br>Expensive Reactants<br>Expensive (Capital)<br>Low Throughput<br>Safety (with group V hydrides) |
| OMVPE | Versatile<br>Uniform<br>Abrupt Interfaces<br>High Purity<br>High Throughput | Expensive Reactants<br>Most Parameters to Control Accurately<br>Safety (with group V hydrides) |

Fig. 1: Overview of epitaxial techniques for the growth of III/V materials.

| Compound/<br>Structure | OMVPE | MBE | CBE | LPE | ClVPE | HVPE |
|---|---|---|---|---|---|---|
| GaAs<br>(77-K) | 205 | 220 | 63 | ———— >200 ———— | | |
| InP<br>(77-K) | 264 | 55 | 154 | 140 | 130 | 75 |
| GaAs/AlGaAs<br>2DEG<br>(<2-K) | $7 \times 10^6$ | $10^7$ | | | | |

Fig. 2: Summary of electron Mobilities ($cm^2/Vs \cdot 10^{-3}$) reported for III/V materials and structures grown by the various epitaxial techniques. Most of the data are from ref. 2. The updated values are from publications referenced in the text.
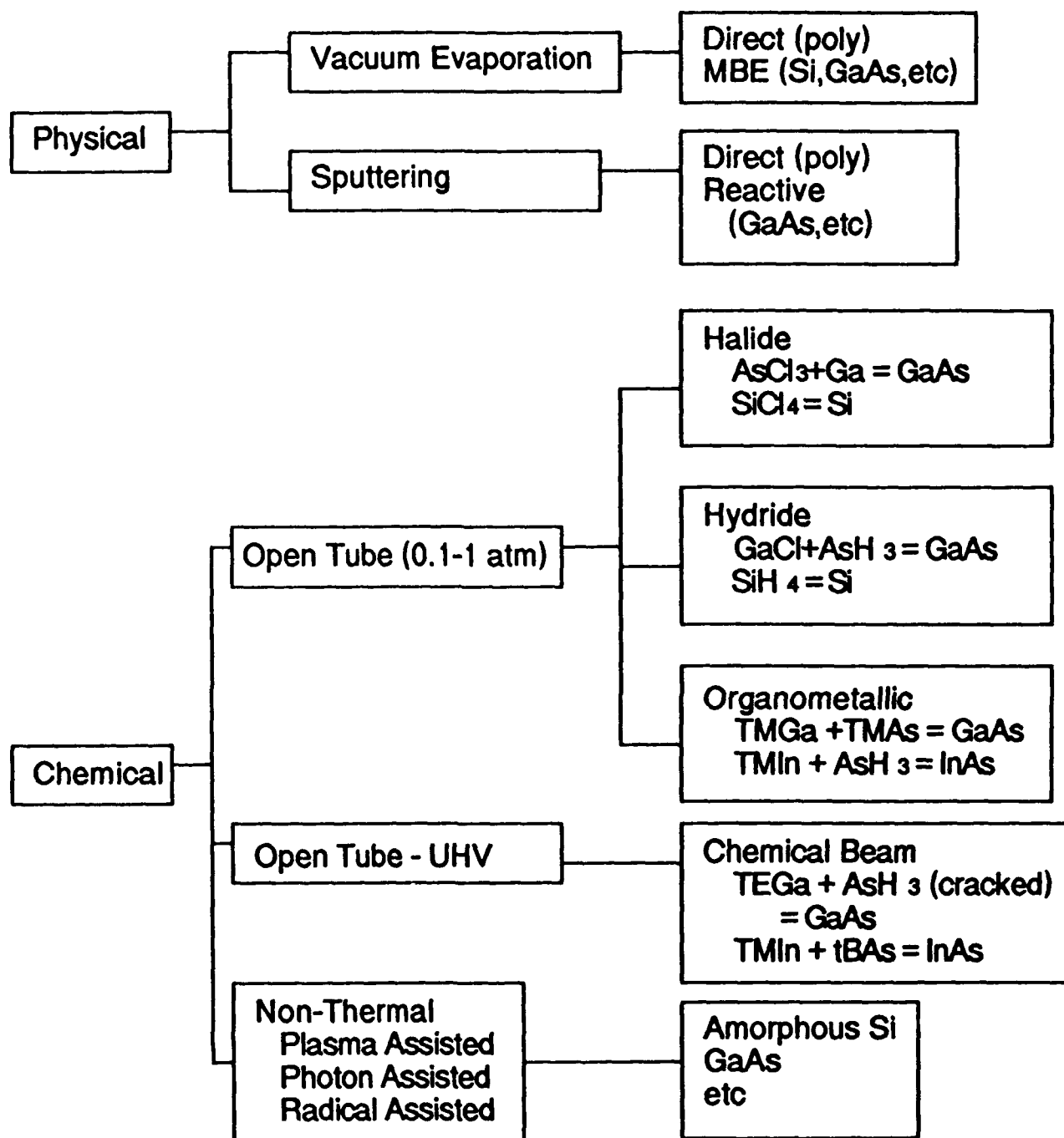
Fig. 3: Schematic illustration (not all inclusive) of the various VPE processes used for the production of III/V materials.

4

involves a discussion of the group III and group V precursor molecules containing the desired group III and group V element plus one or more of the radicals H, Cl, $CH_3$ (methyl), $C_2H_5$ (ethyl), $C_3H_7$ (propyl), $C_4H_9$ (butyl), and others. In fact, the traditional distinctions between the techniques, described above and in Fig. 3, is purely on the basis of the radicals used for the group III and group V molecules. More recently, we have entered the period of "designer" precursors. Thus, for particular applications we might use precursors with both organic radicals and Cl or H. Examples are diethylgalliumchloride (DEGaCl) useful for selected area growth[3] and atomic layer epitaxy (ALE)[4], tertiarybutylarsine (tBAs), a less hazardous substitute for arsine,[5] and trimethylamineallane (TMAA), an aluminum source that gives less carbon contamination than the standard trimethylaluminum (TMAl)[6]. The group III hydrides would be very desirable sources for vapor growth since organic radicals frequently result in carbon contamination of the epitaxial layers, as described below. However, the group III hydrides are too unstable. TMAA was designed to resolve this problem by making an adduct compound with trimethylamine to stabilize the alane.

These examples show that the distinctions between the various vapor phase growth techniques have become blurred as new, hybrid molecules have been adopted. This distinction is further blurred by hybridization such as that between OMVPE and MBE yielding CBE, MOMBE, and GSMBE. A more rational basis for distinguishing the various vapor growth techniques might be the reactor pressure and whether the system has hot or cold walls. Each combination of these features will probably require a different set of characteristics for the precursor molecules. More specialized techniques such as ALE, selective growth, and photon assisted growth will have even more specific requirements. However, it is possible to make a list of the generally desirable features of a precursor, as in Figure 4. For the purposes of this review, the traditional designations of the various vapor phase epitaxial techniques will be retained for coherency and simplicity.

The first requirement of a precursor is that it be sufficiently volatile to allow acceptable epitaxial growth rates. The vapor pressures, along with other properties, are tabulated for group V precursors in Table I. The second requirement is that heating to the desired growth temperature cause pyrolysis. The percent decomposition versus temperature results obtained using an isothermal, flow-tube reactor[7] for several precursors are compared in terms of the values of $T_{50}$, the temperature for 50% pyrolysis under the specific conditions used, in Table I. The relative values of $T_{50}$ are basically a reflection of the strength of the weakest metal-radical bond in the precursor molecule[2]. Arsine ($AsH_3$) and trimethylarsine (TMAs) pyrolyze at the highest temperature since both the H-As and methyl-As bonds are relatively strong. Tertiarybutylarsine (TBAs) decomposes at temperatures more than 200°C less than for arsine because of the weak t-butyl-As bond. The nature of the radicals is also the most important factor determining carbon incorporation. Methyl radicals are quite reactive, so frequently lead to carbon incorporation into the growing solid, especially for Al-containing materials[8]. Less reactive radicals, such as t-$C_4H_9$, apparently result in very little carbon contamination. Ethyl radicals are also much less likely than $CH_3$ to introduce carbon into the solid[9].

5

# GROUP III

## Liquid -- Non Pyrophoric

| OMVPE | CBE |
|---|---|
| High Volatility<br>(1Torr/20C) | Moderate Volatility |
| High Stability (Normally)<br>(No Parasitic Reactions) | Low Stability<br>(Pyrolysis in one Bounce) |
| Low Stability for Low<br>  Temperature Growth | |
| $CH_3$ Radicals<br>Avoid if Possible | No $CH_3$ Radicals |

# GROUP V

## Low Hazard -- Liquid and Non-Toxic

| | |
|---|---|
| High Volatility<br>(50 Torr/20 C) | Moderate Volatility |
| Low Stability<br>(200-400 C) | Very Low Stability<br>(Pyrolysis in one Bounce) |
| Source of H Radicals<br>(Yields $MH_x$ -x=1,2<br>M=P, As, Sb) | Source of H Radicals<br>($MH_x$ from Cracker) |
| No $CH_3$ Radicals | No $CH_3$ Radicals |
| <$15/gram | Cost Less Important<br>(More efficient) |

Fig. 4: Summary of the requirements for precursors to be used in the epitaxial growth of III/V materials.

Table I: Properties of group V sources used for epitaxy. The values of vapor pressure and toxicity were obtained from ref. 2, unless otherwise indicated. The pyrolysis temperatures ($T_{50}$) were obtained from similar experiments in an atmospheric-pressure, flow-tube reactor with a residence time of a few seconds.

| Precursor | Vapor Pressure p.Torr/T.°C | $T_{50}$(°C) | Toxicity $LC_{50}$** (TLV*) | Carbon Doping TMGa/TMIn |
|---|---|---|---|---|
| PH3 | | 850 | 11-50 (0.3) | Very Low |
| TBP | 141/10 | 450 | >1100 | Low |
| AsH3 | | 600 | 5-50 (0.05) | Very Low |
| TMAs | 238/20 | 530 | 20,000 | Very High |
| TEAs | 5/20 | 490 | 500-1000*** | High |
| DMAs | 176/0 | 460 | 130 | High |
| DEAs | 40/20 | 440 | 300 | Low |
| EAs | 145/-7[a] | 440 | | Low |
| TBAs | 96/10 | 380 | 70 | Very Low |
| PhAsH2 | 1.8/20[b] | | | High |
| (C6H5)AsH2 | | | | |

* TLV based on average eight hour work day
** Based on study of rat mortality after 4 hour exposure
***Oral dose in mg of material per kg of animal weight.
a) D.M. Speckman and J.P. Wendt, J. Crystal Growth 105, 275 (1990).
b) A. Brauers, O. Kayser, R. Kall, H. Heinecke, P. Balk, and H. Hofmann, J. Crystal Growth 93, 7 (1988).

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Cl doping is apparently not a problem for III/V semiconductors. H radicals actually act to reduce carbon by supplying the H to convert methyl radicals to virtually inert methane[2].

The above discussion of pyrolysis temperature and carbon contamination is somewhat naive, since it implicitly assumes that pyrolysis occurs by homolysis (or heterolysis), i.e., by the sequential elimination of radicals from the parent molecule until the element is incorporated into the solid. For this process, the bond strength determines the pyrolysis temperature and the nature of the resulting radicals largely determines the rate of carbon incorporation into the growing solid. However, the pyrolysis processes may be considerably more complex, as discussed in the last paper. Here we will simply note that other pyrolysis processes may occur more rapidly than homolysis and produce no reactive radicals. β-elimination reactions[2] occur without radical production, so are favorable for avoiding carbon incorporation, but do not occur for methyl radicals. Pyrolysis of TMAs is believed to occur via hydrogenolysis[10]. In this process, an $H_2$ molecule interacts directly with the TMAs resulting in the production of $CH_4$ plus $(CH_3)_2AsH$. The rate of this process is not determined by the As-$CH_3$ bond strength and no $CH_3$ radicals are produced. The ambient can also interact with radicals produced by homolysis to reduce carbon

7

contamination. The highly reactive methyl radicals react with an $H_2$ ambient to produce methane and reactive, potentially beneficial, H radicals[2].

The major factor driving the initial stages of the search for improved precursor molecules was the demand for less hazardous precursors. Arsine and phosphine are extremely dangerous because of their toxicity combined with their high vapor pressures of many atmospheres. Liquid, organometallic sources are approximately 100X less hazardous solely due to their lower vapor pressures, resulting in slower dispersal into the atmosphere, which, in turn, leads to lower concentrations in case of an accidental release of the precursor into the atmosphere of the laboratory[2]. Fortunately, many organometallic molecules are also considerably less toxic than the hydrides. The outstanding example is tertiarybutylphosphine (TBP), with a toxicity orders of magnitude lower than that for phosphine. Available toxicity data are also included in Table I.

The leading candidates for replacement of the P and As hydrides are TBP and either TBAs or ethylarsine (EAs). All of these molecules yield fairly stable organic radicals during pyrolysis. They also produce $MH_2$ radicals, where M is either As or P, that act to remove organic radicals from the surface. Thus, carbon contamination appears not to be a problem. In fact, recent data on the growth of GaAs and AlGaAs by OMVPE using TBAs indicates lower carbon concentrations than for growth using arsine[11].

## IV. CHLORIDE VAPOR PHASE EPITAXY

ClVPE was the other leading technique (in addition to LPE) for the epitaxial growth of III/V semiconductors during the 1960's and 70's. Again, high purity GaAs layers were obtained due to the availability of high purity $AsCl_3$, a liquid which is easily purified using conventional techniques. As seen in Fig. 2, the GaAs and InP purities obtained by ClVPE are comparable to those produced by LPE. The purity levels have not advanced significantly in over a decade, due to the relatively minor research activity devoted to ClVPE. This is partially due to the inability to grow Al-containing alloys using this technique, due to thermodynamic factors involving the relative stabilities of the Al and Ga chlorides[12]. In addition, the production of abrupt interfaces by ClVPE has proven to be extremely difficult. The rather cumbersome "multibarrel" technique[13] of moving the substrate between multiple tubes containing the required chemical flows for the growth of the various alloys required in a quantum well or superlattice structure has not proven capable of producing the required level of interface abruptness.

More promising is vapor levitation epitaxy(VLE), where the substrate is shuttled between positions in the reactor where a flow of the required gasses passes upward through an $SiO_2$ frit[14]. The gas flow suspends the substrate above the frit, giving a uniform, thin boundary layer for mass transport to the growing surface. This results in excellent uniformities in both thickness and composition. It also allows the rapid movement of the wafer from one frit to another for rapid changes in composition, equivalent to moving the substrate from one tube to

8

another in the "multibarrel" technique described above. This gives interface abruptnesses of <10Å. In spite of the promising results, this technique is not widely utilized, probably due to the complexity and fragility of the VLE apparatus and the success achieved by competing techniques such as MBE, OMVPE, GSMBE, MOMBE, and CBE.

## V. HYDRIDE VAPOR PHASE EPITAXY

The growth of GaAsP using HCl passed over heated Ga to produce GaCl, combined with arsine and phosphine, was the first large-scale epitaxial production technique for III/V semiconductors. It was used for the production of GaAsP light emitting diodes during the 1970's and is still in use at the present time. The purification of the group V hydride gasses proved to be much more difficult than for liquid $AsCl_3$. In addition, the HCl reacts with the stainless steel of the apparatus as well as the hot $SiO_2$ walls, producing contamination of the growing layer. As a result, high purity GaAs and InP were obtained much later than for the two techniques discussed above. Today, 77K electron mobilities of >200,000 $cm^2/Vs$ have been obtained for GaAs, but the InP purity is still inferior to that obtained using other techniques.

## VI. MOLECULAR BEAM EPITAXY

MBE and OMVPE were developed in approximately the same time frame, in the late 1960's and early 70's. MBE progressed more rapidly due to the simplicity inherent in the use of elemental sources. The ultra-high vacuum ambient also resulted in relatively high purity layers, although the push to produce extremely high purity GaAs has succeeded only relatively recently, after herculean efforts[15]. The use of elemental phosphorus presents difficulties with MBE, as indicated in Fig. 1. This is partially due to the inability to trap the excess P: It normally ends up in the pumping systems. Thus, the InP purity levels indicated in Fig. 2 are much poorer than for the other techniques. Even the production of InP with with 77K electron mobilities of 55,000 $cm^2/Vs$ is a difficult, non-routine task[16].The control of composition in As/P alloys has proven to be even more difficult in MBE[17].

A serious difficulty with MBE is the occurrence of so-called "oval" defects during growth of GaAs and AlGaAs.[18] MBE was the early leader in the quest for a production technique for high performance HEMT devices. However, the production of high-yield medium- and large-scale integrated circuits requires lower surface defect densities than can be obtained by MBE. An additional difficulty for large-scale production applications is the difficulty in up-scaling an UHV apparatus to allow the simultaneous growth on multiple wafers with the required uniformity. In addition, the apparatus is inherently extremely expensive.

The great advantage of MBE is the ability to produce atomically abrupt changes in composition and/or doping and the resulting superlattice structures. MBE allowed the pioneering efforts in device research using quantum well, 2 dimensional electron gas, and superlattice structures. Without MBE the resulting

9

revolution in device performance would have been delayed. An area in which MBE remains virtually unchallanged is the use of in-situ techniques to monitor, and thus understand, the epitaxial growth process. Using RHEED techniques, the growth process can be observed as it proceeds layer by layer[19]. This has provided the basis of a much more profound understanding of the epitaxial processes occurring in MBE. This knowledge has also allowed significant advances in our insights into similar fundamental steps in other VPE techniques, as well.

## VII. ORGANOMETALLIC VAPOR PHASE EPITAXY

OMVPE was the last of the "standard" VPE techniques to reach maturity. This is largely due to the complexity of the technique. To really understand and control OMVPE requires an understanding of the basic characteristics of organometallic and hydride precursors, including an understanding of homogeneous and heterogeneous pyrolysis reactions. Only recently has the body of information necessary to understand these processes reached the size necessary to provide significant input into understanding the overall process.

This very area, that has retarded the development of OMVPE, now provides a significant advantage relative to other, competing epitaxial growth techniques. New precursor molecules are being developed at a rapid rate. The motivation is to increase the power of OMVPE to produce specific materials and/or structures. For example, for low temperature growth a number of more labile In, As, P, and Sb precursors have been developed recently[20]. This has allow the growth temperature to be reduced to as low as 275C[21]. Specific precursors are also being developed to allow selective growth, i.e., only in the mask openings on a III/V substrate surface and for ALE. In the future, it appears likely that specific precursors will also be developed for photon assisted growth as well as for UHV techniques such as MOMBE, GSMBE, and CBE. With complexity comes power and versatility. OMVPE is the most versatile epitaxial growth technique. It can apparently be used for the production of virtually every III/V alloy. This includes those having miscibility gaps, as discussed in the last paper.[22]

Another major factor retarding the development of OMVPE has been the inability to escape carbon contamination, especially in Al-containing alloys. Again, the development of novel precursor molecules has proved to be the key to the solution of this problem. The use of TMAA, discussed above, has led to the reduction of carbon contamination in AlGaAs to acceptable levels. Closely coupled with this has been the development of novel group V precursors that release $MH_2$ radicals on the growing surface, as discussed above. Again, the development of novel precursors, such as TBAs, EAs, and TBP, has significantly reduced the safety hazard associated with OMVPE growth. This factor plays a major role in determining which epitaxial technique will be used in manufacturing applications. The use of highly hazardous materials significantly increases the operating expenses. It also adds unacceptable uncertainties for a manufacturing operation, especially in light of the emotional approach evidenced by the public in assessing the danger of such a facility in a highly populated area.

10

A final point related to the organometallic precursors is the high operating expense. The high cost of TBAs and TBP has prevented their use in some, extremely cost-sensitive applications. Fortunately, as the usage increases, the cost decreases, as for all semiconductor operations. Apparently, this threshold has been exceeded. The new precursors are finding acceptance in manufacturing operations which has resulted in a noticable decrease in price.

Other advantages of OMVPE are well documented. It has been proven successful in multi-wafer reactors, with excellent uniformity of thickness and solid composition[18,23]. In recent years, OMVPE has also been proven capable of producing heterostructures, quantum wells, and superlattices with approximately atomically-abrupt interfaces[24]. The purity levels achieved in recent years are perhaps the best of all techniques, since the InP purity[25] far exceeds that obtained by any of the other techniques. Very recently, OMVF⊑ has challenged MBE even in the area of 2 dimensional electron gas mobilities[26], although MBE still retains a slight edge[27].

## VIII. MBE-OMVPE HYBRID TECHNIQUES

The latest development in epitaxial growth techniques has been the hybridization of OMVPE with MBE, resulting in UHV techniques using combinations of elemental, organometallic, and hydride sources. In conventional terminology[28] GSMBE uses elemental group III sources combined with either hydride or, more recently, organometallic group V sources. MOMBE (or OMMBE) involves the use of elemental group V sources and organometallic group III sources. CBE might be considered a very low pressure form of OMVPE, since it uses organometallic group III sources combined with either hydride or organometallic group V sources in a UHV reactor. These hybrid techniques retain several of the advantages of MBE, such as the ability to produce atomically abrupt interfaces and in-situ monitoring of the process, with the associated control of the process. The use of organometallic (and hydride) sources has significantly increased the versatility of MBE, especially for P- and Sb-containing materials. For example, the 77K electron mobiltiy of CBE-grown InP is comparable to the results produced by other techniques, as seen in Fig. 2.

With these advantages come some of the problems associated with OMVPE, namely the use of expensive and, in some cases, extremely hazardous precursors. The problems with carbon contamination are exacerbated in CBE, since the group V sources are typically cracked before reaching the growing surface. Thus, even though the starting materials may be the group V hydrides, no atomic hydrogen is carried to the surface. Thus, methyl radicals from the group III precursors typically result in unacceptable levels of carbon contamination in GaAs and AlGaAs. The use of triethyl-gallium and aluminum results in less carbon contamination. However, the use of TMAA has produced even better results. Unfortunately, the Ga analogue of TMAA is probably too unstable to be used for OMVPE. However, it may be useful for CBE[29]. Again, it is anticipated that novel group V precursors can be used to carry atomic H to the

11

surface under the proper conditions. This is expected to give more flexibility in the choice of group III precursors.

CBE has a few disadvantages, even with the use of optimized precursors. Combining MBE and OMVPE results in the most expensive apparatus, with research reactors running at well over 1 million U.S. dollars. The throughput appears to be limited by the UHV chamber. OMVPE remains the leading technique for the production of large quantities of material. However, CBE is significantly better than MBE, since the group V source chamber need not be routinely opened to atmosphere for re-charging. This step requires periodic bake-outs for MBE systems.

IX. SUMMARY

In terms of purity, the 77K mobilities for thick layers of both GaAs and InP using the various epitaxial growth techniques are remarkably comparable. The first 77 K GaAs mobilities exceeding 100,000 $cm^2/Vs$ were obtained using the CIVPE and LPE techniques. The lack of high purity precursors delayed achieving this purity level in materials grown by HVPE and OMVPE. Today, all the growth techniques have demonstrated extremely high mobilities, with the exception of the rather low purity levels obtained for InP grown by MBE.

Remarkable low temperature mobilities exceeding $10^7$ $cm^2/Vs$ have recently been reported for GaAs/AlGaAs two dimensional electron gas structures grown by MBE. This requires both extremely high purity GaAs as well as abrupt and smooth GaAs/AlGaAs interfaces. Even more recently, similar mobilities have been measured in structures grown by OMVPE. The ability to grow abrupt interfaces, leading to quantum well and superlattice structures, was first demonstrated using MBE. Although it took years to develop, comparable interfaces are now produced by OMVPE and CBE. None of the other epitaxial techniques described here (LPE, CIVPE, and HVPE) are capable of growing such abrupt interfaces with the possible exception of the specialized CIVPE technique, vapor levitation epitaxy. The rather crude techniques where the substrate is shuttled back and forth between chambers, such as for LPE or the multibarrel vapor phase epitaxy reactors, are much less effective in producing such structures.

In terms of interfacial recombination velocities, another measure of the quality of interfaces, OMVPE has recently been proven to be superior, with values of interface recombination velocity for GaAs/AlGaAs interfaces as low as 40 cm/sec[26]. These values are much better than those measured for structures grown by MBE and measured in the same laboratory, and are at least as good as those reported for similar structures grown by LPE.

The standard measure of perfection for thick epitaxial layers is the minority carrier lifetime. High lifetimes signify a low density of non-radiative recombination centers. Again, GaAs grown by LPE first demonstrated minority carrier lifetimes of approximately 1 µs. The measurement of such long lifetimes requires the use of sophisticated structures to avoid recombination at the top

surface and the substrate/epilayer interface. Using such structures, GaAs grown by OMVPE has recently yielded minority carrier lifetimes exceeding 14 μs[30]. These are the highest reliable lifetimes ever reported for GaAs. Similar structures grown by MBE gave numbers in excess of 1 μs, but not as high as the materials grown by OMVPE.

Finally, every one of the epitaxial growth techniques described has found a nitch and is used for the production of a particular material, structure, and/or device. Nevertheless, much of this status is due to the history of the development of the growth techniques, with LPE, CIVPE, and HVPE maturing much earlier than either OMVPE or MBE. For the modern quantum well, two dimensional electron gas, and superlattice structures that have revolutionized device design and performance, only the latter two techniques, plus the hybridized techniques such as CBE, have demonstrated the requisite capabilities. Thus, most epitaxy research effort during the last 5 years has been devoted to the OMVPE, MBE, and hybrid techniques. Again, each will find its nitch in production. However, the versatility and capability for large scale production already demonstrated for OMVPE make it the favorite to assume the role as the work-horse production technique of the future.

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